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(54) Process for preparing polysacharides containing hydrophobic side chains

(57) The invention relates to a process for preparing a hydrophobically modified polysaccharide as well as to the preparation of a liquid detergent composition comprising such polysaccharide material.

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Description

Technical Field

The present invention relates to a process of preparing polysaccharides that contain one or more hydrophobic sidechains as well as to the preparation of a liquid detergent composition comprising such polysaccharide material.

Background & Prior Art

Hydrophobically modified (HM) polysaccharides are well-known in the art, as well as process for making such saccharides.

US 2,661,349 describes a process in which polysaccharides are converted with substituted cyclic dicarboxylic acid anhydrides to form ester compounds. The document describes that the conversion process can be carried out in an aqueous environment or according to a dry method. A third method describes the use of an organic suspension or dispersion of the polysaccharide. The suspended or dispersed particles of polysaccharide will only be able to react on the surface.

US 4,035,235 describes a method of making hydrophobically modified starch derivatives by esterification of the starch with n-octenyl succinic anhydride in an aqueous environment. The starch derivatives contains from about 0.1 to 10% by weight of anhydride, based on the dry weight of starch.

HM polysaccharides can be used for various purposes, including food and detergent products. One of such uses is their applications in liquid detergent compositions comprising a structure of lamellar droplets as e.g. described in EP 346,995, EP 505,371 and GB 2,256,646, where they are called deflocculating polymers.

We have found a particular way to prepare hydrophobically modified polysaccharides that results in more clearly defined modified polysaccharides. We have further found that the resulting polysaccharides have the additional benefit of showing good deflocculating properties in lamellar structured liquids.

Statement of the Invention

The invention provides a process for preparing polysaccharides with one or more hydrophobic sidechains by preparing a mixture of polysaccharide, hydrophobic chain containing compound and solvent material, said mixture comprising at most 25% by weight of water, characterised in that the polysaccharide is dissolved.

Optionally, the mixture also contains a base material.

The invention further provides a process for preparing an aqueous liquid detergent composition comprising lamellar droplets of surfactant material and a polysaccharide with one or more hydrophobic sidechains, by mixing water, surfactant material and said polysaccharide material, wherein said polysaccharide material is prepared by preparing a mixture of polysaccharide, hydrophobic chain containing compound and solvent material, wherein said mixture comprises at most 25% by weight of water and wherein the polysaccharide is in a dissolved state.

Description of the Invention

Without wishing to be bound by any theory, it is believed that the process of the present invention leads to a homogeneous reaction mixture and the hydrophobic sidechains will be homogeneously distributed between all sugar units that are available for bonding with the hydrophobic compound. This results in a homogeneous distribution of the hydrophobic side-chains, not only within each polysaccharide molecule, but also between the various molecules. It is believed that such homogeneous distribution is beneficial to the use of the hydrophobically modified polysaccharides, i.e. they are better defined, which is e.g. useful when they are used as deflocculating polymers in lamellar structured liquid detergent compositions.

Polysaccharides

Polysaccharides that can be used in the process of the present invention may be selected from pentose and hexose ring structures, e.g. starch, (gelatinized or ungelatinized; degraded; from any source: corn, tapioca, potato, wheat, sago, rice, waxy maize, dextrins), cellulose, hemi-cellulose, inuline, dextran and levan. Preferred compounds are starch, inuline, fibrulin, dextran, sinistrin and pullulan.

Preferably the polysaccharide is present at a level of 10 to 90% by weight of the reaction mixture.

Preferably the polysaccharide have a weight average molecular weight in the region of from 500-500,000, preferably 750-100,000, most preferably 1,000 to 30,000, especially from 2,000 to 10,000, when measured by GPC using polyacrylate standards, as measured by the absolute intrinsic viscosity method described by Noda, Tsoge and Nagasawa in Journal of Physical Chemistry, Volume 74, (1970), page 710-719.

Hydrophobic Chain Containing Compound

Hydrophobic chain containing compounds that may be used in processes of the present invention are C6-C24 alk(en)yl containing compounds, e.g. C6-C24 alk(en)yl succinic anhydride material. Preferably, the alk(en)yl chain is at least C8, more preferably at least C9 and preferably the alk(en)yl chain is at most C22, more preferably at most C18. Optionally, the anhydride material contains from 1 to 50 poly(oxyethylene) groups between the alk(en)yl chain and the succinic anhydride group.

Preferably the hydrophobic chain containing compound is present at a level of 0.01 to 25%, more preferably 0.1 to 15%, most preferably 1 to 10% by weight of the reaction mixture.

Solvent

Solvents that may be used in processes of the present invention may be selected from materials in which the polysaccharide is soluble. Preferred solvents are selected from Di-Methyl Formamide, Di-Methyl Sulf-Oxide, pyridine, N-methyl imidazole, acetonitrile, tetrahydrofuran, aceton and mixtures thereof.

Preferably, the solvent is present at a level of 10 to 90%, more preferably 20 to 80%, most preferably 30 to 70% by weight of the reaction mixture.

Base material

Optionally, the reaction mixture also contains a base material. This material may be selected from any material that has a 1% pH in water at ambient temperature of higher than 7. Preferably the base material is selected from pyridine, N-methyl imidazole, dimethylamino pyridine, sodium or potassium hydroxide, sodium or potassium carbonate. It will be understood that other base material that is suggested in the art for use in acid anhydride-alcohol reactions, may also be used in the reaction of the present invention.

Preferably the base material is present at a level of 0 to 90%, more preferably 5%-80%, most preferably at least 10-70% by weight of the reaction mixture.

Reaction mixture

Preferably, the water level in the reaction mixture is at most 25% by weight, more preferably at most 20% by weight, most preferably at most 15% by weight, in particular at most 10% by weight.

Preferably, the weight ratio between the polysaccharide and the hydrophobing compound is from 4:1 to 1000:1, more preferably from 6:1 to 250:1, most preferably 10:1 to 100:1.

Preferably, the weight ratio between the polysaccharide and the solvent is lower than 200:1, more preferably lower than 50:1. Preferably, the weight ratio is higher than 1:100, more preferably higher than 1:50, most preferably higher than 1:20, in particular 1:10, e.g. higher than 1:4.

The polysaccharide is homogeneously mixed with the solvent material and the hydrophobic chain containing compound.

Preparation Process

Surprisingly, it has been found that when the polysaccharide is dissolved in a low water reaction mixture, the polysaccharide material becomes substituted with hydrophobic sidechains which are homogeneously distributed between the groups on the sugar units that are available for bonding with the hydrophobic compound. We have found that these conditions lead to a homogeneous distribution of the hydrophobic side-chains within each polysaccharide molecule as well as between the various polysaccharide molecules results. Such compounds are in particular beneficial for use as deflocculating polymers in lamellar structured liquid detergent compositions.

The process temperature is preferably held between 25 and 125°C, although at higher temperatures (at least 55, more preferably at least 75, most preferably at least 85°C) the results are better. Preferably, the temperature is at most 115, more preferably at most 105, most preferably at most 95°C.

The polymer can thereafter be purified by evaporation of the solvent or by precipitation, e.g. by using diethyl ether, methanol or preferably by using aceton.

Hydrophobically Modified (HM) Polysaccharide

Preferably, the degree of substitution (DS; the number of hydrophobic groups per sugar unit) is from 0.001 tot 0.20, more preferably from 0.01 to 0.10.

Preferably the HM polysaccharide contain on average at least 0.1, more preferably at least 0.2, most preferably at least 0.5 and preferably at most 3, more preferably at most 2 anchors per polysaccharide molecule.

Identification of the HM polysaccharide - DS

The degree of hydrophobic modification is expressed as the degree of substitution (DS) and is defined as the amount of anchors per monosaccharide unit. For polymers of hexose-sugars the maximum DS is 3 since there are 3 free OH-groups per monosaccharide unit.

In the ^{1}H-NMR spectrum the signals deriving from the polysaccharide and the alk(en)yl chain are quite different. Using the integral from these signals, the number of alk(en)yl chains that are present can be easily calculated and the DS is calculated (it is assumed that all alk(en)yl chain present is covalently bound to the polysaccharide which assumption was thought to be reasonable because the products obtained were carefully washed with solvents that are very good solvents for the starting alk(en)yl reagents or possibly formed side-products. Also further washing had no effect on the calculated DS so it was quite likely that indeed the alk(en)yl chains were covalently bound to the polysaccharide).

Identification of the HM polysaccharide - Molecular Weight

The molecular weight of the polysaccharides (DP) is expressed as the degree of polymerization (DP = number of monosaccharide units). This value will always be an averaged number. Molecular weight determinations are normally made using gel permeation chromatography (GPC) techniques. For inulin ^{1}H-NMR spectroscopy, ion-exchange chromatography or a Dionex column may be used.

Liquid characteristics

Polymer that are prepared according to the present invention may be used in liquid detergent compositions comprising lamellar droplets of surfactant material.

A preferred form of lamellar structures are lamellar droplets of surfactant material. The dispersed structuring phase in such liquids is generally believed to consist of an onion-like configuration comprising concentric bilayers surfactant molecules, between which water is trapped, the aqueous phase. Liquids with a lamellar droplets structure provide a very desirable combination of physical stability and solid-suspending properties with useful flow properties, i.e. low viscosity with stability. Such liquids have for example been described in A. Jurgens, Microstructure and Viscosity of Liquid Detergent, Tenside Surfactants Detergent 26 (1989) 222 and J.C. van de Pas, Liquid Detergents, Tenside Surfactants Detergents 28 (1991) 158.

The presence and identity of a surfactant structuring system in a liquid may be determined by means known to those skilled in the art for example, optical techniques, various rheometrical measurements, X-ray or neutron diffraction, and sometimes, electron microscopy.

Liquids with lamellar droplets including the kind and level of ingredients have been described in EP 346,995 and GB 2,256,646. These two documents are herewith incorporated herein by reference.

Liquids with lamellar droplets generally comprise from 10-70% by weight of surfactant material, from 1-60% by weight of electrolyte material, from 10-60% by weight of water and may further comprise from 1-5% by weight of the HM polysaccharide material of the invention.

Aqueous liquid detergent composition comprising lamellar droplets of surfactant material may be prepared by mixing of water and surfactant material, optionally in the presence of electrolyte material. The polysaccharide material with one or more hydrophobic sidechains may be added before, during or after the mixing.

The invention will be illustrated by way of the following non-limiting Examples.

Examples

Example - Comparison between no and low solvent reactions

Reaction with no solvent:

Dodecenyl succinic anhydride (1.3 g) and 4-dimethylamino pyridine (1.3 g) were dissolved in 100 ml of dichloromethane. This solution was added to inulin (24 g) in a round bottomed flask. The solvent was quickly removed in vacuo. The reaction flask was than placed in such a way that it could be horizontally rotated and a homogeneous mixing could be performed. The flask was than heated to 130°C and the mixture reacted for 2 hours. After cooling the reaction mixture was poured in acetone. After filtration and drying 22 g product was obtained, which had (according to ^{1}H-NMR) a DS = 0.02.

Low solvent reaction:

A mixture of inulin (25 g; 154 mequivalents), dodecenyl succinic anhydride (1.5g; 6 mmol), pyridine (1g) and dimethyl formamide (15g DMF) was mixed and heated to 80-90°C. After about 20 minutes a clear homogeneous and very viscous reaction mixture was obtained. This mixture was stirred for 3 hours at about 85°C. The mixture was poured in acetone and the product was obtained after filtration and drying (the product can also be obtained by evaporating the solvent). 27 g product was obtained, which according to ^{1}H-NMR had a DS = 0.03.

The results of the synthese is listed in the table as well as the viscosity and flocculation degree of liquids with lamellar droplets of surfactant material containing the polysaccharides with the hydrophobic sidechains.

TABLE

Inulin Floccul. mequiv [1]	DSA [2] mmol	DS [3] found	Inul/ DMF [4] w/w	Anchors/ molecule	Visc. [5] mPas at at 21 s^{-1}	Degree [6]
148	5	0.02	no solvent	0.7	240	fl
92.5	6	0.02	0.15	0.8	40	sfl
154	6	0.03	0.5	1.0	110	pfl
154	6	0.02	1	0.7	140	pfl
154	6	0.02	1.68	0.8	140	pfl

1) Expressed as hexose units; ex Inuline dahlia
2) Dodecenyl Succinic Acid
3) DS is degree of substitution
4) Di-Methyl-Formamide (DMF)
5) Viscosity resulting after addition of the HM inuline to a lamellar structured liquid that was prepared by dissolving 20 parts of electrolyte in 60 parts of water, whereafter 40 parts of active and 1 part of polymer was added. The liquid without the HM inuline is strongly flocculated, unstable and its viscosity is about 3000.
6) As observed by light microscopy, wherein
fl = flocculated
sfl = slightly flocculated
pfl = partly flocculated

Claims

1. Process for preparing polysaccharides with one or more hydrophobic sidechains by preparing a mixture of polysaccharide, hydrophobic chain containing compound and solvent material, said mixture comprising at most 25% by weight of water, characterised in that the polysaccharide is dissolved.

2. Process according to claim 1, characterised in that the solvent is selected from Di-Methyl-Formamide, Di-Methyl-Sulfoxide, pyridine, N-methyl imidazole, acetonitrile, tetrahydrofuran, aceton and mixtures thereof.

3. Process according to claim 1, characterised in that the hydrophobic chain containing compound has a C8-C20 alk(en)yl chain.

4. Process according to claim 1, characterised in that the polysaccharide is selected from starch, degraded starch, cellulose, hemi-cellulose, inuline, dextran and levan.

5. Process according to claim 1, characterised in that the polysaccharide with one or more hydrophobic sidechains has a degree of substitution of 0.001 to 0.2.

6. Process for preparing an aqueous liquid detergent composition comprising lamellar droplets of surfactant material and a polysaccharide with one or more hydrophobic sidechains, by mixing water, surfactant material and said polysaccharide material, wherein said polysaccharide material is prepared by preparing a mixture of polysaccharide, hydrophobic chain containing compound and solvent material, wherein said mixture comprises at most 25% by weight of water and wherein the polysaccharide is in a dissolved state.

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EUROPEAN SEARCH REPORT

Application Number
EP 95 20 2556

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DATABASE WPI Week 8915 Derwent Publications Ltd., London, GB; AN 109357 & JP-A-01 054 001 (SUGIYAMA SANGYOKAGA) , 1 March 1989 * abstract * & PATENT ABSTRACTS OF JAPAN vol. 13 no. 249 (C-605) ,9 June 1989 * abstract * & CHEMICAL ABSTRACTS, vol. 111, no. 8, 21 August 1989 Columbus, Ohio, US; page 115; column 59893g; * abstract *	1-6	C08B37/00 C08B31/04 C11D17/00 C11D3/39
D,Y	WO-A-91 09109 (UNILEVER PLC) * page 9 - page 11 *	1-6	
Y	MAKROMOLEKULARE CHEMIE, MACROMOLECULAR CHEMISTRY AND PHYSICS, vol. 187, no. 1, 1 January 1986 BASEL CH, pages 125-131, JOAN VERMEERSCH ET AL. 'Synthesis and characterization of inulin monosuccinates' *page 126, Results*	1-6	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C08B C11D
Y	US-A-4 906 744 (PEUSCHER ET AL.) 6 March 1990 * column 1, line 50 - column 2, line 55 *	1-6	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 December 1995	Lensen, H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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